Exhibit 63

PageID: 222663

PageID: 222664

Journal of Molecular Structure 1140 (2017) 67–70

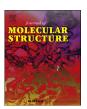
Document 33016-3

EL SEVIED

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc



Linear birefringence of polymer foils determined by optical means



Adina Elena Scripa (Tudose)*, Dan Gheorghe Dimitriu, Dana Ortansa Dorohoi

Faculty of Physics, "Alexandru Ioan Cuza" University, 11 Carol I Blvd., RO-700506 Iasi, Romania

ARTICLE INFO

Article history: Received 14 December 2016 Accepted 22 December 2016 Available online 23 December 2016

Keywords: Linear birefringence Foils polymer Channeled spectra Optical anisotropy

ABSTRACT

An interferential method is used for determining the linear birefringence of the thin polymer foils. The channeled spectra of anisotropic polyethylene terephthalate (PET) transparent films, placed between two identical crossed polarizers were recorded and the linear birefringence was estimated by using the conditions of the minima and maxima of flux density in the channeled spectrum. This method is very fast, allowing the estimation of the linear birefringence over the entire visible range from a single recording of the channeled spectrum. The obtained results are consistent with those previously reported in the literature.

© 2016 Published by Elsevier B.V.

1. Introduction

Birefringence is an optical property of some materials which have refractive index dependent on the polarization and propagation direction of light. The birefringence is quantified as the maximum difference between refractive indices of the material. The most common birefringent materials are the crystals (including here the liquid crystals) with asymmetric structures and the plastics under mechanical stress.

For uniaxial materials there is a single direction governing the optical anisotropy (called as optic axis of the material), whereas all directions perpendicular to it are optically equivalent. The uniax materials are characterized by two values of the refractive index. The ordinary value (n_0) is measured with linearly polarized radiations acting perpendicular on optical axis, while the extraordinary value (n_e) corresponds to linearly polarized radiations with their electric field intensity parallel to the optical axis. The difference between the two refractive indices gives the value of the linear birefringence:

$$\Delta n = n_e - n_0 \tag{1}$$

Optical birefringence is classified as positive when the extraordinary index of refraction n_e is greater than the ordinary index of refraction n_o , and as negative in the opposite case.

The biaxial materials are characterized by three refractive indices. In this case, there are two different extraordinary

* Corresponding author.

E-mail address: adinascripa@yahoo.com (A.E. Scripa (Tudose)).

refractive indices. Thus, there is no axis around which a rotation leaves the optical properties invariant, as in the case of uniaxial materials.

Polyethylene terephthalate (PET) is the most common thermoplastic polymer resin of the polyester family, being used in fibers for clothing, containers for liquids and foods, thermoforming for manufacturing and, in combination with glass fibers, for engineering resins [1]. PET consists of polymerized units of the monomer ethylene terephthalate, with repeating C₁₀H₈O₄ units. In its natural state, PET is colorless, very lightweight and impact-resistant. Biaxially-oriented polyethylene terephthalate (BoPET) is a polyester film made from stretched PET and used for its high tensile strength, chemical and dimensional stability, transparency, reflectivity, gas and aroma barrier properties and electrical insulation [2]. From optically point of view, PET behaves in the first approximation as a uniaxial material, because the two extraordinary refractive indices have very close values [3,4].

Here, a method to determine the birefringence of a polymer foil which allows us evaluating its values for the entire visible spectrum in a fast way is used [5]. The method consists in recording the channeled spectrum of a transparent polymer foil. Channeled spectrum is a succession of maxima and minima of the flux density resulting from the phase difference introduced between light components propagating with different velocities. This method was previously validated for thin layers of liquid crystals [6,7], or quartz [5,8] to determine the linear birefringence, being later extended to polymer solutions [9–11] for the estimation of optical rotatory dispersion.

A.E. Scripa (Tudose) et al. / Journal of Molecular Structure 1140 (2017) 67-70

PageID: 222665

Document 33016-3

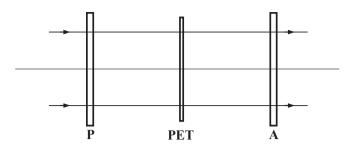


Fig. 1. Experimental device used to record the channeled spectra.

2. Experimental setup

The experimental setup used for linear birefringence determination is schematically shown in Fig. 1. The device consists of two identical polarizers (P and A), between which the PET foil is introduced as an anisotropic layer. The two polarizers are crossed (they have perpendicular transmission directions). By using visible light, the birefringence of the PET foil can be estimated from the channeled spectra, which are recorded with an Ocean Optics QE65000 spectrophotometer with data acquisition system. A $(30 \times 30 \text{ mm})$ PET foil of 0.125 mm thickness was purchased from Goodfellow.

3. Theoretical background

The device is illuminated with visible light. The polarizer P transforms the radiation into a linearly polarized one, with its electric field intensity parallel to polarizer transmission direction. The transparent PET foil of a thickness (L) introduced a phase difference $\Delta \phi$ between the ordinary and extraordinary rays given

$$\Delta \phi = \frac{2\pi}{\lambda_0} \Delta nL \tag{2}$$

The linear birefringence is a dispersive parameter like the refractive indices. The method of channeled spectra permits the determination of the linear birefringence and of its dispersion in a large spectral range for which the polymer foil is transparent. When the phase difference introduced between the ordinary and extraordinary rays is an even $2k\pi$, $k=1, 2 \dots$ number of π , the polarization state does not change and the corresponding components of light do not pass through the second polarizer. When the phase difference between ordinary and extraordinary components is an odd $(2k+1)\pi$ number of π , the electric field intensity of the emergent light from the polymer plate becomes parallel to the second polarizer and can pass through it with maximum of flux density.

The transmission factor of the device (defined as the ratio between the light flux measured after the polarizer A and the light flux at the entrance of the polymer foil) can be written as [10,11]:

$$T = \sin^2 \frac{2\pi}{\lambda_0} \, \Delta nL \tag{3}$$

Relation (3) is obtained for the crossed polarizers P and A, and for principal axes of the foil making an angle of $\frac{\pi}{4}$ with the transmission direction of the polarizers.

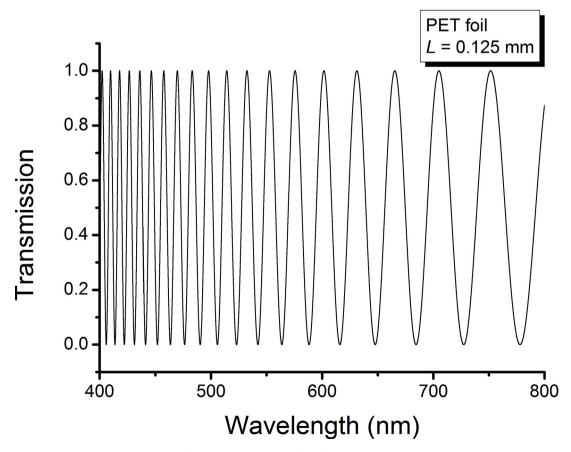


Fig. 2. Channeled spectrum of PET foil (L = 0.125 nm).

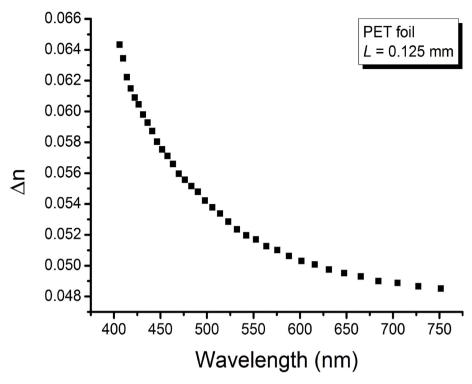


Fig. 3. Birefringence of PET foil as a function of wavelength.

When a source of visible radiations is used to illuminate the polymer foil, the device from Fig. 1 introduces phase differences between ordinary and extraordinary components which depend on

the wavelengths and a channeled spectrum as that from Fig. 2 is recorded with spectrophotometer.

The wavelengths in the maxima $\lambda_{k+1/2}$ and minima λ_k of the

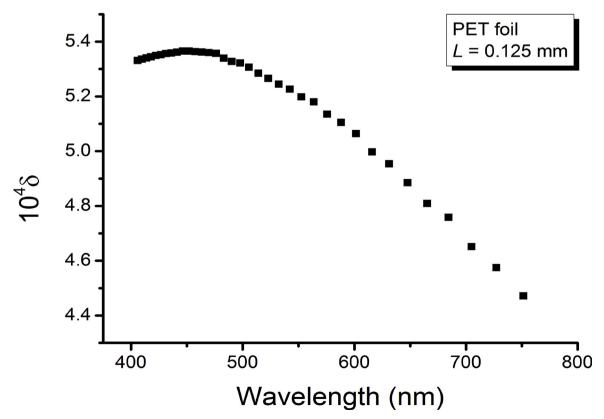


Fig. 4. Dispersive parameter for PET foil as a function of wavelength.

PageID: 222667

Document 33016-3

70

channeled spectrum are used to determine the birefringence Δn at a given wavelength and its dispersion, expressed by the a-dimensional parameter δ (variation of Δn from a channel of order k to the neighbor maximum of order k+1/2, situated towards lower wavelengths in the visible range). The formulas were previously established [12]:

$$\Delta n = \frac{1}{2L} \frac{\lambda_{k+1} \lambda_2 (\lambda_k - \lambda_{k+1})}{\lambda_{k+1} - 2\lambda_{k+1} \lambda_2 + \lambda_k}$$
(4)

$$\delta = \frac{1}{2L} \frac{2\lambda_{k+1}\lambda_k - \lambda_{k+1/2}(\lambda_{k+1} - \lambda_k)}{\lambda_{k+1} - 2\lambda_{k+1/2} - \lambda_k}$$
 (5)

These formulas are efficient for materials with small values of the dispersive parameter. They allow us to estimate the linear birefringence and the birefringence dispersion by using the wavelengths of two consecutive minima and the maximum between them, or two consecutive maxima and the minimum between them, respectively, from the channeled spectrum.

4. Results and discussion

The channeled spectrum of PET foil of about 0.125 mm thickness is shown in Fig. 2. The number of channels in the spectrum depends on both the birefringence and thickness of the polymer foil. From experimental data the birefringence Δn and the dispersive parameter δ as depending on the wavelength are plotted and shown in Figs. 3 and 4.

From Fig. 3 it results a decrease of PET birefringence with increasing the light wavelength. The obtained values for the birefringence are in good agreement with the previously reported ones [13]. The dispersive parameter is not a characteristic of PET foil. Its dependence on the light wavelength demonstrates that the initial supposition of constant value is not valid in the visible range. Anyway, because the values of the dispersive parameter are approximately 100 times smaller than that one of the birefringence, we still consider that the obtained results have enough precision.

5. Conclusions

The method of channeled spectrum is applied here for the estimation of the linear birefringence of polymer (PET) foils. This method has the advantage that permits measurements over the entire visible domain of the wavelengths in a fast way, by performing only one experiment. The birefringence of PET foil decreases with the increasing of the light wavelength.

The hypothesis that the dispersive parameter is a constant parameter is the visible range is not validated, but due to its very small values the method can be used for estimating the linear birefringence.

References

- [1] G. Wypych, Handbook of Polymers, Chem Tec Publishing, Toronto, 2012.
- [2] M.T. DeMeuse, Biaxial Stretching of Film. Principles and Applications, Woodhead Publishing Limited, Cambridge, 2011.
- [3] B.M. Johnson, Relaxation of PET Orientation at Temperatures below the Glass Transition, MSc. Thesis, University of Toledo, MSin Chemical Engineering, College of Engineering, 2013.
- [4] T. Wakayama, Y. Otani, N. Umeda, Opt. Commun. 281 (2008) 3668–3672.
- [5] D.G. Dimitriu, D.O. Dorohoi, New method to determine the optical rotatory dispersion of inorganic crystals applied to some samples of Carpathian quartz, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 131 (2014) 674–677.
- [6] D.O. Dorohoi, M. Postolache, M. Postolache, Birefringence dispersion of poly (phenyl methacrylic) ester of cetyloxybenzoic acid in tetrachloromethane determined from channeled spectrum, J. Macromol. Sci. Part B Phys. 40 (2001) 239–249
- [7] S. Picos, G. Amarandei, I. Diaconu, D.O. Dorohoi, The birefringence on thin films of some nematic liquid crystals, J. Optoelectron. Adv. Mater. 7 (2005) 787–793
- [8] D.O. Dorohoi, D.G. Dimitriu, I. Dumitrascu, C.B. Zelinschi, I. Breaban, Interferential method to determine the optical rotatory dispersion of crystalline layers, Univ. Politehnica Buchar. Sci. Bull. Ser. A Appl. Math. Phys. 77 (2015) 253–260.
- [9] A.I. Barzic, D.G. Dimitriu, D.O. Dorohoi, New method for determining the optical rotatory dispersion of hydroxypropyl cellulose polymer solutions in water, Polym. Eng. Sci. 55 (2015) 1077–1081.
- [10] A.I. Barzic, D.G. Dimitriu, D.O. Dorohoi, Optical activity of polymer solutions studied by visible electron spectroscopy, Int. J. Polym. Anal. Charact. 20 (2015) 565–571.
- [11] A.I. Cosutchi, D.G. Dimitriu, C.B. Zelinschi, I. Breaban, D.O. Dorohoi, Optical activity of transparent polymer layers characterized by spectral means, J. Mol. Struct. 1090 (2015) 39–43.
- [12] V. Pop, Ed. Univ. "Al. I. Cuza" Iasi, Optica, (1988) (in Romanian).
- [13] K.L. Mittal, Polymer Surface Modification: Relevance to Adhesion, vol. 4, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2007.